THE ANNALS OF THE AGRICULTURAL COLLEGE OF SWEDEN
Vol. 9, 1941.

The acid-base condition in vegetation, litter and humus: I. Acids, acidoids and bases in relation to decomposition.[1]

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From the Institute of Pedology.

The ashes of plants are alkaline because they contain bases in excess of mineral acids. This means that the plants are pumping up bases from the lower to the upper horizons of the soil. But vegetation and litter contain an excess of organic acids and acidoids and react therefore more or less acidic. Acids and acidoids may also be formed and accumulated during the decomposition of the litter. Whether or not the plants will increase or decrease the acid/base ratio in the soil will, therefore, depend on the nature and intensity of the decomposition. The acid-base balance becomes a balance between the production of organic acids and acidoids and the leaching of bases on the one side and the destruction of the organic acids and acidoids and the base pumping power of the plants on the other side.

The aim of the present work, which was started three years ago, was to study the acid-base balance in plant materials during various stages of transformation and under various conditions in the laboratory and in nature. Several contributions have been made on the total base, the excess base and the Ca content and on the acidity and the buffer capacity of various types of litter (1, 2, 3, 5, 6). The present work differs from that of previous workers in that we determine the acids and acidoids separately in addition to the bases.

Laboratory experiments.

Flower pots of about two liters capacity were provided with a bottom outlet consisting of glass and rubber tubing with clamp.

[1] This work is supported by funds from the Royal Swedish Academy of Agriculture.

A convex piece of tinned wire netting (12 meshes/inch) was placed over the opening. The pots were then filled with hot paraffin until impregnated.

One hundred grams of the air dry plant material (cf. table 1) were placed in each of the pots, moistened with destilled water, inocculated with an extract of garden soil and forest humus and covered with a piece of fibre plate.

The experiment included the following series:

1. Aerobic series with no leaching. Moistened every week.
2. Aerobic series. Moistened every week and leached with sufficient water to yield 100 cc every other week.
3. The same as 2 but leached with 400 cc.
4. Anaerobic series. No leaching. The material was kept constantly under water.

Table 1. *Description of vegetation (V) and litter F (= förna) used in the pot experiments.*

Name	Sample	Location	Date collected
Picea excelsa	V Spruce needles	Ultuna woods[1]	April 1936
Pinus silvestris	F_0[2] Pine »	» »	Nov. 1935
Fagus silvatica	F_0 Beech leaves	Hallandsås[3]	» »
Betula pubescens	F_0 Birch »	Ultuna park[4]	» »
Fraxinus excelsior	F_0 Ash »	» »	» »
Alnus incana	F_0 Alder »	» »	» »
Ulmus glabra	F_0 Elm »	» »	» »
Quercus robur	F_0 Oak »	» »	» »
Acer platanoides	F_0 Maple »	» »	» »
Vaccinium myrtillus	V Blueberry leaves	» woods	July 1936
Vaccinium vitis idaea	V Whortleberry leaves	» »	» »
Pleurhozium parietinum	V Whole plant	» »	Nov. »
Cetraria islandica	V Whole plant	Norrland	» »
Gramineae spp.[5]	Faded tops	Ultuna park	» »
Triticum vulgare	Wheat straw	Ultuna farm	Aug. 1935
Medicago sativa	Lucern hay	» »	July 1936

[1] Gravelly soil in places slightly podzolized.
[2] We have adopted Hesselman's symbols for the F and H layers but with the modification that we denote the recently fallen, unaltered förna by F_0, the partly decomposed but uppermost and hence less than one year old förna by F_1 and the older and more decomposed förna by F_2, F_3 etc. down to the amorphous humus H (or H_1, H_2 etc.).
[3] Brown earth with low base status.
[4] River clay with high base status.
[5] Avena elatior, Dactylis glomerata, Poa pratensis, Triticum repens, Phleum pratense.

5. The same as 4 but 100 cc were withdrawn every two weeks.
6. The same as 4 but 400 cc were withdrawn every two weeks.

The experiments were carried on for one year. During this time 24 leachings were obtained amounting to 2 400 cc from each pot of the series leached with 100 cc and to 9 600 cc from the series leached with 400 cc. The temperature was that of the laboratory.

Analytical methods.

The pH was determined by the quinhydrone method in a 1:10 suspension of the ground material in water.

The acidity (H) was found by electrometric titration of the original material to pH 7.

The bases (B) were determined as »excess base» by a backward titration to methyl orange of the ash obtained by gentle ignition in the electric furnace.

Table 2. *The pH of the leachings in the 400 cc series.*[1]

Material	Original	Weeks 1	2	4	8	12	16	20	28	36	44	52
Aerobic:												
Picea excelsa	4.32	4.89	6.45	6.74	7.05	7.01	6.88	6.96	6.75	6.96	7.20	7.16
Pinus silvestris	4.22	5.08	5.54	5.78	6.28	6.43	6.70	6.77	6.43	6.18	5.89	5.28
Fagus silvatica	5.08	5.81	6.38	7.02	7.18	7.38	7.30	7.04	6.93	6.73	6.73	6.94
Betula pubescens	5.99	6.83	7.64	7.70	7.61	7.60	7.61	7.65	7.56	7.53	7.41	7.46
Fraxinus excelsior	6.24	7.85	7.85	7.72	8.20	7.95	8.03	7.81	7.58	7.65	7.50	7.57
Alnus incana	4.89	5.23	6.53	7.30	7.93	8.25	7.81	7.07	6.95	7.07	6.78	6.89
Ulmus glabra	5.91	7.96	7.86	7.67	7.90	7.91	8.03	7.84	7.75	[2]		
Quercus robur	4.48	4.77	5.17	5.64	6.21	6.29	6.18	6.54	7.26	7.25	7.36	7.31
Acer platanoides	4.49	4.66	5.31	5.97	6.48	7.00	7.08	7.29	7.65	7.68	7.82	7.77
Vaccinium myrtillus	3.97	3.97	4.64	4.99	6.78	6.97	7.43	7.65	6.62	6.27	6.28	6.37
Vaccinium vitis idaea	4.93	4.98	4.98	4.71	5.58	5.96	5.88	5.71	6.09	6.44	6.51	6.58
Pleurhozium parietinum	4.71	5.43	6.23	6.99	7.14	6.74	6.84	6.98	6.90	6.54	6.60	6.10
Cetraria islandica	4.89	5.18	6.37	6.12	5.70	6.01	6.00	5.98	5.73	5.72	[2]	
Gramineae	5.59	6.31	7.56	7.34	6.91	7.03	6.97	6.90	6.67	6.65	6.59	6.45
Triticum vulgare	6.14	7.79	7.84	7.80	7.46	7.42	7.45	7.32	7.26	7.12	6.94	7.15
Medicago sativa	5.40	7.68	8.83	8.73	8.50	8.39	7.87	7.59	7.72	7.73	7.84	7.65
Anaerobic:												
Picea excelsa	4.32	4.49	3.93	3.96	4.14	4.64	5.20	5.76	6.59	7.09	6.99	6.77
Pinus silvestris	4.22	4.51	4.36	4.43	4.72	5.08	5.36	5.44	5.84	6.33	6.27	6.54
Fagus silvatica	5.08	5.40	4.95	5.04	5.42	6.38	6.47	6.73	6.79	7.00	6.78	7.11
Betula pubescens	5.99	6.03	5.03	5.03	5.52	5.91	5.85	5.73	5.75	5.96	5.89	5.85
Triticum vulgare	6.14	5.89	4.76	4.61	4.70	4.68	4.68	4.60	4.58	4.69	4.77	4.78
Medicago sativa	5.40	5.09	5.69	5.41	5.19	5.13	5.37	5.65	7.19	6.99	7.25	7.25

[1] Only 11 of the 24—400 cc leachings are included in this table.
[2] Would not drain.

The acidoids (*A*) were determined by electrometric titration of the completely electrodialysed material to pH 7.

The organic acids (*a*) are put equal to the difference: acidity + excess base — acidoids or:

$$H + B - A = a.$$

The acid/base balance is then expressed by the ratio:

$$\frac{A + a}{B}$$

or in terms of H and B by the ratio:

$$\frac{H + B}{B}$$

which makes electrodialysis and the estimation of acidoids unnecessary.

The ultimate pH (pH_u) or the pH of the completely electrodialysed material has been obtained both in water and in N.KCl.

The exchange acidity is the difference between the pH_u in water and the pH_u in the KCl solution.

Table 3. *The loss on ignition and the ash content in the leachings. The sum of 24 extracts obtained during one year.*

Gram per 100 g. original material.

Material	Aerobic				Anaerobic			
	Loss on ignition		Ash		Loss on ignition		Ash	
	Leachings cc:							
	2400	9600	2400	9600	2400	9600	2400	9600
Picea excelsa	0.846	1.830	0.377	0.665	9.860	13.170	1.654	1.965
Pinus silvestris	1.055	2.749	0.190	0.436	3.392	5.234	0.658	0.950
Fagus silvatica	2.492	4.190	0.652	1.338	2.289	3.667	1.138	2.223
Betula pubescens	2.087	3.654	1.296	2.177	4.557	8.222	2.824	4.175
Average	1.620	3.106	0.629	1.154	5.025	7.573	1.569	2.328
Fraxinus excelsior	3.772	7.641	1.745	3.259				
Alnus incana	9.652	16.146	1.243	1.756				
Ulmus glabra	2.391	5.171	1.393	3.458				
Quercus robur	2.319	4.780	0.892	1.589				
Acer platanoides	2.994	5.595	1.364	2.232				
Vaccinium myrtillus	—	28.571	—	2.666				
Vaccinium vitis idaea	—	4.452	—	0.618				
Pleurhozium parietinum	—	5.710	—	1.981				
Cetraria islandica	3.012	5.110	0.123	0.185				
Gramineae	—	6.708	—	1.655				
Triticum vulgare	—	4.032	—	2.077		6.203		2.771
Medicago sativa	7.434	10.876	3.269	4.051		21.723		5.806

Table 4. *Excess acids in the leachings and excess base in the ashes. The sum of 24 extract obtained during one year.*

Milliequivalents/100 gram.

Material	Aerobic:				Anaerobic:			
	Acids		Bases		Acids		Bases	
	Leachings cc:							
	2400	9600	2400	9600	2400	9600	2400	9600
Picea excelsa	0.13	0.71	4.01	6.48	37.59	40.08	24.88	28.22
Pinus silvestris	0.44	1.77	3.08	8.03	9.76	18.49	12.78	19.24
Fagus silvatica	0.30	0.67	7.93	9.70	2.42	8.53	13.53	16.95
Betula pubescens	0.03	0.09	18.94	36.04	13.77	26.97	56.13	88.37
Average	0.23	0.81	8.49	15.06	15.89	23.52	26.83	38.20
Fraxinus excelsior	0.00	0.00	22.26	54.87				
Alnus incana	0.86	1.32	28.29	38.98				
Ulmus glabra	0.00	0.00	23.86	63.45				
Quercus robur	2.18	3.71	8.93	15.95				
Acer platanoides	0.95	2.59	18.00	26.12				
Vaccinium myrtillus		12.13		44.06				
Vaccinium vitis idaea		3.30		6.25				
Pleurhozium parietinum		1.31		27.67				
Cetraria islandica	2.52	1.59	0.91	1.94				
Gramineae		0.37		18.61				
Triticum vulgare		0.00		19.17		37.34		31.84
Medicago sativa	0.00	0.00	36.37	55.59		46.94		150.32

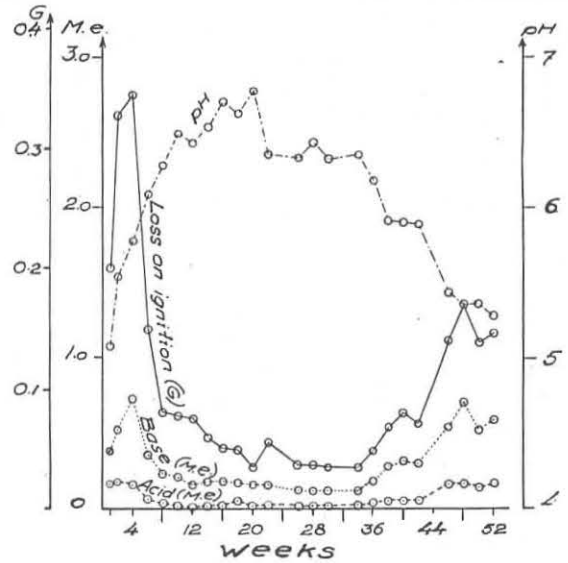

Fig. 1. Composition and pH of the 400 cc fortnightly leachings. Pine needles. Aerobic.

It should be pointed out that the equivalent ratio of acids to bases is something which can only be very indefinitely related to the actual acid-base conditions. This is especially true of systems containing acids and acidoids of widely varying strength. This ratio is not only affected by the pH to which the acids and acidoids are titrated. It depends also on the base we use in the titration and on the composition and concentration of the solution. Thus an acidoid binds more $Ca(OH)_2$ than NaOH, other things being equal, and binds, at a given pH, more base the higher the cation activity of the solution, the effect of the divalent cations being relatively much greater in dilute solutions than that of the monovalent (MATTSON & WIKLANDER, 1940). The apparent dissociation constants of the acidoids vary, therefore, considerably and this causes the acid-base relationships to vary accordingly. This behavior must have important consequences in the physiology of plant and animals.

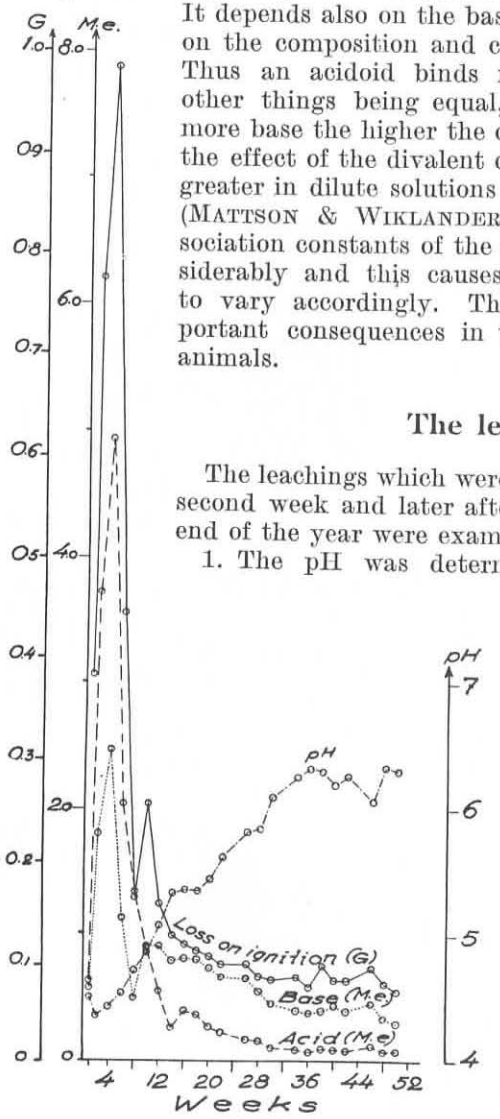

Fig. 2. Same as fig. 1. Pine neddles. Anaerobic.

The leachings.

The leachings which were obtained after the first and second week and later after every two weeks until the end of the year were examined as follows:

1. The pH was determined by the quinhydrone method.
2. The free acids when present in the leachings were electrometrically titrated to pH 7.0.
3. The loss on ignition and ash content were determined by gentle ignition over a Fisher burner.
4. The excess base in the ash was titrated backwards to methyl orange.

pH: Table 2 gives the pH in 11 of the 24 leachings in the 400 cc series.

We note in the aerobic series that the pH increases rapidly, in many cases up to and above the neutral point. The highest pH values (>8) are found in the

case of lucern, ash, elm and alder whereas the pH in the leachings from the more acidic materials remains below 7. After a certain maximum is attained the pH begins to fall. We shall see later that the initial increase in pH is due to the destruction of the

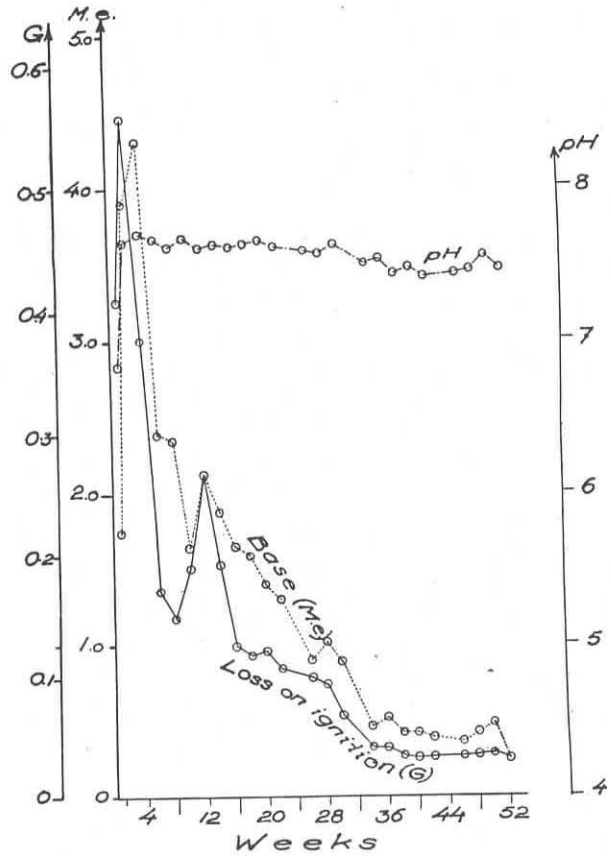

Fig. 3. Same as fig. 1. Birch leaves. Aerobic.

organic acids whereas the subsequent decrease is due (1) to the leaching of bases and (2) to a production of humus acidoids.

In the anaerobic series there is an initial decrease and, with the exception of straw, a subsequent increase in pH. The decrease is due to the production of organic acids from easily fermentable carbohydrates. These acids are, as we shall see, later decomposed as a result of which the pH again increases. The »anaerobic» conditions in our experiment are, of course, far from being strictly anaerobic.

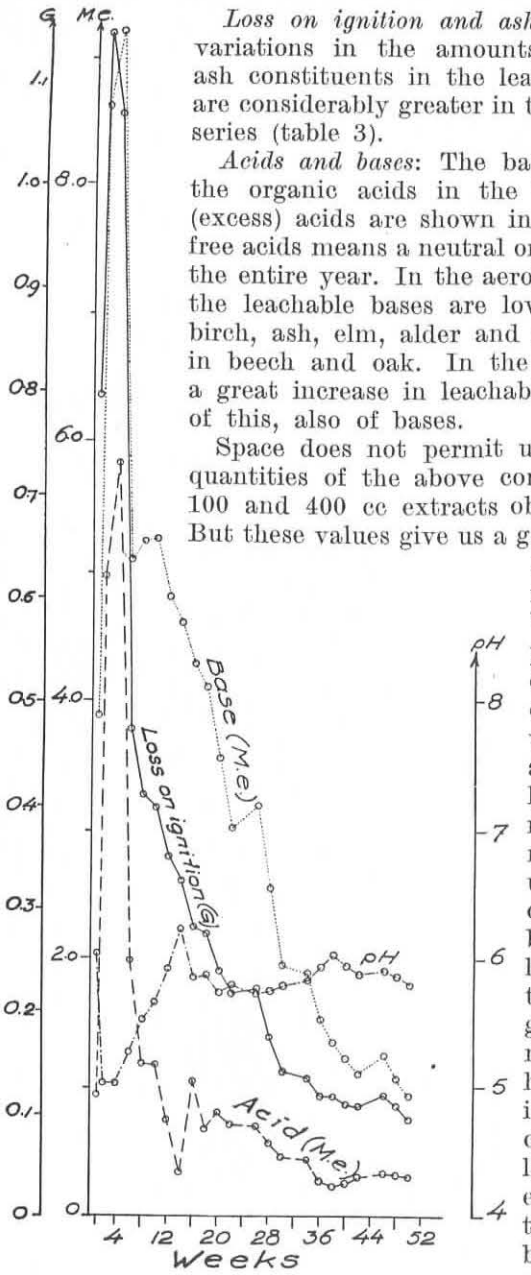

Fig. 4. Same as fig. 1. Birch leaves. Anaerobic.

Loss on ignition and ash content: There is great variations in the amounts of organic matter and ash constituents in the leachings but both of these are considerably greater in the more acidic anaerobic series (table 3).

Acids and bases: The bases in combination with the organic acids in the leachings and the free (excess) acids are shown in table 4. The absence of free acids means a neutral or alkaline reaction during the entire year. In the aerobic series of F_0 materials the leachable bases are lowest in pine, highest in birch, ash, elm, alder and maple and intermediate in beech and oak. In the anaerobic series we find a great increase in leachable acids and, as a result of this, also of bases.

Space does not permit us to give the individual quantities of the above components in each of the 100 and 400 cc extracts obtained during the year. But these values give us a good insight into the first and most rapid transformation of the material. We shall therefore graphically show the process of leaching in the case of two of the F_0 materials under aerobic and anaerobic conditions, namely, birch leaves and pine needles (fig. 1—4). These materials might be looked upon as representatives of the types to which they belong. We note that the leaching of organic matter and bases is very great during the first months. This fact must have an important bearing on podzolization in cold countries where the litter is subjected to an extensive leaching during the cold season before it becomes food for the microorganisms. In warm countries the microbes

get their food fresh whereas in cold countries they get it leached and therefore less easily digested. Hence the tendency to accummulate.

Transformed residue.

Dry matter: At the end of the year the residue was dried in the air, weighed and ground to a powder.

Table 5 shows the amount of dry matter per pot before and after the transformation.

The decomposition is greater in the aerobic than in the anaerobic series and if the leachings (in table 3) are added to the residue it will be found that the decomposition is in every case greater in the unleached than in the leached series, the difference being most marked in the anaerobic series. The percentage decomposition will be discussed later.

The loss on ignition (table 6) has decreased in the leached as well as in the unleached aerobic series whereas it has increased in the leached anaerobic series. It might therefore be said that the aerobic

Table 5. *Dry material (105° C.) per pot at the beginning and at the end of 1 year.*

Grams.

Material	Original	Transformed: Aerobic: Leachings cc: None	Aerobic: 2400	Aerobic: 9600	Anaerobic: None	Anaerobic: 2400	Anaerobic: 9600
Picea excelsa	93.1	51.7	56.0	51.8	70.6	67.0	64.6
Pinus silvestris	91.3	50.2	47.4	43.3	75.4	74.9	73.6
Fagus silvatica	92.1	53.2	48.3	44.9	79.3	78.6	76.7
Betula pubescens	91.2	43.7	42.8	43.0	70.1	64.7	66.0
Average 4:	91.9	49.7	48.6	45.8	73.9	71.3	70.2
Fraxinus excelsior	88.9	32.5	29.8	26.2			
Alnus incana	89.1	47.2	38.3	30.7			
Ulmus glabra	88.7	44.3	42.7	38.7			
Quercus robur	90.1	51.6	48.3	46.3			
Acer platanoides	90.1	43.8	42.7	40.7			
Vaccinium myrtillus	91.6	37.4	—	20.0			
Vaccinium vitis idaea	92.0	47.5	—	43.7			
Pleurhozium parietinum	90.2	59.5	—	35.6			
Cetraria islandica	88.2	38.2	47.2	49.1			
Gramineae	92.5	27.2	—	21.4			
Triticum vulgare	90.0	52.0	—	49.7	60.4		73.2
Medicago sativa	89.3	24.9	15.5	15.0	42.4		29.6
Average 16:	90.5	44.1	—	37.5			

Table 6. *Percentage loss on ignition of the original and the transformed material on the basis of dry matter.*

(100—% loss on ignition = % ash.)

Material	Original	Transformed:					
		Aerobic:			Anaerobic:		
		Leachings cc:					
		None	2400	9600	None	2400	9600
Picea excelsa	96.29	93.47	94.71	94.99	96.41	98.05	98.39
Pinus silvestris	97.30	95.37	95.20	95.20	96.54	97.51	97.89
Fagus silvatica	93.66	90.30	89.49	90.22	93.39	94.58	95.53
Betula pubescens	92.22	85.68	89.04	87.65	91.62	94.62	96.11
Average 4:	94.87	91.20	92.11	92.01	94.49	96.19	96.98
Fraxinus excelsior	86.31	69.42	68.70	71.58			
Alnus incana	93.40	89.68	90.17	88.97			
Ulmus glabra	73.47	51.41	51.09	51.35			
Quercus robur	92.66	88.08	88.08	89.26			
Acer platanoides	89.22	78.72	80.08	81.90			
Vaccinium myrtillus	95.44	89.01		91.45			
Vaccinium vitis idaea	97.37	95.23		96.05			
Pleurhozium parietinum	94.79	91.84		88.56			
Cetraria islandica	99.03	97.04	98.41	98.05			
Gramineae	92.54	78.25		78.16			
Triticum vulgare	89.55	82.87		87.55	84.54		90.03
Medicago sativa	87.29	67.82	65.36	68.86	79.36		97.69
Average 16:	91.91	84.01		84.99			

transformation is dominated by the decomposition whereas the anaerobic transformation is dominated by the leaching.

This does not mean that the pH in the leached anaerobic series must decrease as a result of the loss of bases, bacause the acids are leached out at a higher rate than the bases which, to a certain extent, are held by the acidoids. In addition to this it is chiefly the organic acids which are involved in the decomposition once the acid fermentation is over.

The pH values in table 7 (and table 2) can thus be accounted for. These values are in general considerably higher in the transformed than in the original material. In the aerobic series the reaction is alkaline in the case of birch, ash, elm, maple and lucern. The pH is in general lower in the leached than in the unleached series. Important exceptions to this rule are alder, whose pH increases with the leaching, and wheat straw whose pH 5.03 in the last column is over a unit lower than the original pH. This decrease in the pH of the anaerobically transformed straw must be ascribed to a nearly complete leaching of the bases (cf. table 9). As far as the alder is

Table 7. *The pH of the original and the transformed materials.*

Material	Original	Transformed:					
		Aerobic:			Anaerobic:		
		Leachings cc:					
		None	2400	9600	None	2400	9600
Picea excelsa	4.32	6.91	6.79	6.73	6.51	5.88	5.57
Pinus silvestris	4.22	5.96	6.04	4.97	6.08	5.77	5.56
Fagus silvatica	5.08	6.67	6.42	6.26	6.59	6.12	5.89
Betula pubescens	5.99	8.26	7.52	7.09	7.34	6.48	5.65
Average 4:	4.90	6.95	6.69	6.26	6.63	6.06	5.67
Fraxinus excelsior	6.24	7.81	7.67	7.50			
Alnus incana	4.89	5.04	5.89	6.58			
Ulmus glabra	5.91	8.44	8.40	8.03			
Quercus robur	4.48	6.55	6.65	6.68			
Acer platanoides	4.49	7.61	7.52	7.34			
Vaccinium myrtillus	3.97	6.37		6.02			
Vaccinium vitis idaea	4.93	5.75		5.69			
Pleurhozium parietinum	4.71	4.45		5.56			
Cetraria islandica	4.89	5.32	5.22	5.44			
Gramineae	5.39	6.73		5.94			
Triticum vulgare	6.14	7.32		6.15	7.32		5.03
Medicago sativa	5.40	7.81	7.79	7.33	7.51		6.43
Average 16:	5.08	6.69		6.46			

concerned it deserves to be mentioned, especially for the sake of future reference, that both NH_3- and HNO_3-formation was very much in evidence (the former by smell and the latter by flashes when igniting) during the transformation of these leaves (cf. also HESSELMAN 1926). It seems therefore certain that the increase in pH on leaching is due to a removal of HNO_3 which in the unleached alder gives rise to the relatively low pH of 5.04.

The same initial increase and subsequent drop in pH was found in the litter which was decomposing under natural conditions under the same trees under which our materials for the pot experiment were collected. Thus the pH of the litter of birch and oak leaves were in November 5.99 and 4.48, in July 6,78 and 6.87 and in September 5.99 and 5.47 respectively.

The acidity as given in table 8 is obtained by interpolation of the curves in fig. 5 a and 6 a. In all but one case (moss) the acidity has decreased in the anaerobic as well as in the aerobic series. Where no acidity is reported the pH was above 7.

Bases: These are given as found by backward titration of the ashes to methyl orange (table 9). In the original material these values vary between 264.2 m.e./100 g in ash and 8.6 m.e. in the

Table 8. *The acidity (H) of the original and transformed material (by electrometric titration with NaOH to pH 7. Cf. fig. 5 a and 6 a).*

M.e./100 g. dry matter.

Material	Original	Transformed:					
		Aerobic:			Anaerobic:		
		Leachings cc:					
		None	2400	9600	None	2400	9600
Picea excelsa	30.6	0	2.3	2.9	3.8	7.0	8.2
Pinus silvestris	33.9	13.8	11.2	33.6	7.9	10.2	12.5
Fagus silvatica	26.3	6.5	10.4	12.8	7.0	9.4	10.1
Betula pubescens	16.0	—	—	—	—	5.7	15.1
Average 3:	30.3	6.8	8.0	16.4	6.2	8.9	10.3
Fraxinus excelsior	16.2	—	—	—			
Alnus incana	49.2	47.0	18.8	7.3			
Ulmus glabra	25.0	—	—	—			
Quercus robur	47.2	8.3	6.2	5.7			
Acer platanoides	35.0	—	—	—			
Vaccinium myrtillus	70.0	14.3	—	13.2			
Vaccinium vitis idaea	24.1	21.9	—	20.2			
Pleurhozium parietinum	39.4	49.5	—	22.7			
Cetraria islandica	24.8	18.8	19.1	16.9			
Gramineae	21.7	5.4	—	17.6			
Triticum vulgare	9.8	—	—	5.9	—	—	6.2
Medicago sativa	31.5	—	—	—	—	—	5.0
Average 7:	39.5	23.6	—	14.8	—	—	—

lichens. In the unleached series the increase in base content is proportional to the absolute amount of decomposition (deviations from this relationship might, among other things, result from variations in the amounts of sulphur and chlorine lost during ignition). In the leached, aerobic series there is an accumulation of bases whereas in the anaerobic there is a depletion. In the former the acid-base conditions are dominated by decomposition, in the latter by leaching.

Acidoids: In order better to compare the acidoid content in the different materials we have calculated the results on the basis of Loss on ignition (table 10 b) as well as on the basis of dry matter (table 10 a). We note:

1. that the acidoid content attains considerable proportions already in the original materials and that the highest values are associated with a high base content and a high pH (cf. ash and elm tables 9 and 10).

2. that the acidoids increase considerably in the aerobic series especially in the unleached (the lichens which formed an »anaerobic» mass and the rapidly decomposing lucern are exceptions); and

Table 9. *Titrable bases (B) in the ash (by backward titration to methyl orange).*

M.e./100 g. dry matter.

Material	Original	Transformed:					
		Aerobic:			Anaerobic:		
		Leachings cc:					
		None	2400	9600	None	2400	9600
Picea excelsa	45.1	67.8	84.9	71.8	54.0	28.1	21.3
Pinus silvestris	43.2	69.7	71.2	65.7	55.0	36.2	31.5
Fagus silvatica	76.2	112.2	97.5	106.8	86.2	66.8	58.6
Betula pubescens	140.4	245.4	198.8	220.2	151.4	99.2	66.7
Average 4:	76.2	123.8	113.1	116.1	86.7	57.6	44.5
Fraxinus excelsior	264.2	388.4	410.3	395.5			
Alnus incana	90.1	157.5	123.5	142.8			
Ulmus glabra	261.0	409.6	385.0	398.7			
Quercus robur	100.1	177.1	165.8	159.8			
Acer platanoides	136.8	286.0	257.9	244.4			
Vaccinium myrtillus	62.1	159.3		112.4			
Vaccinium vitis idaea	35.9	70.1		58.6			
Pleurhozium parietinum	41.6	67.4		68.9			
Cetraria islandica	8.6	19.5	9.5	13.8			
Gramineae	40.5	98.0		63.3			
Triticum vulgare	39.5	60.5		26.4	54.2		6.1
Medicago sativa	162.8	416.0	450.0	449.9	342.8		28.9
Average 16:	96.8	175.3		162.4			

3. that the anaerobic transformation causes a slight increase in acidoids in the unleached series and a slight decrease in the leached series (in lucern the decrease is great in both series).

Fig. 5 b and 6 b show the titration curves of the electrodialysed, original and transformed (unleached, aerobic series) materials respectively. The curves are based on dry weight as in table 10 a. Note the increase in buffer capacity in the transformed materials. This increase would be still greater if the curves were based on the loss on ignition as in table 10 b.

The organic acids. These are given in table 11 and are put equal to the sum of the acidity H and the bases B minus the acidoids A according to the equation

$$H + B = A + a.$$

Now since H, A and a express the capacity to bind base up to pH 7 only, we cannot apply this equation to alkaline material. The value of a would be too large for such material because B represents here a greater amount of base than that which is necessary to neu-

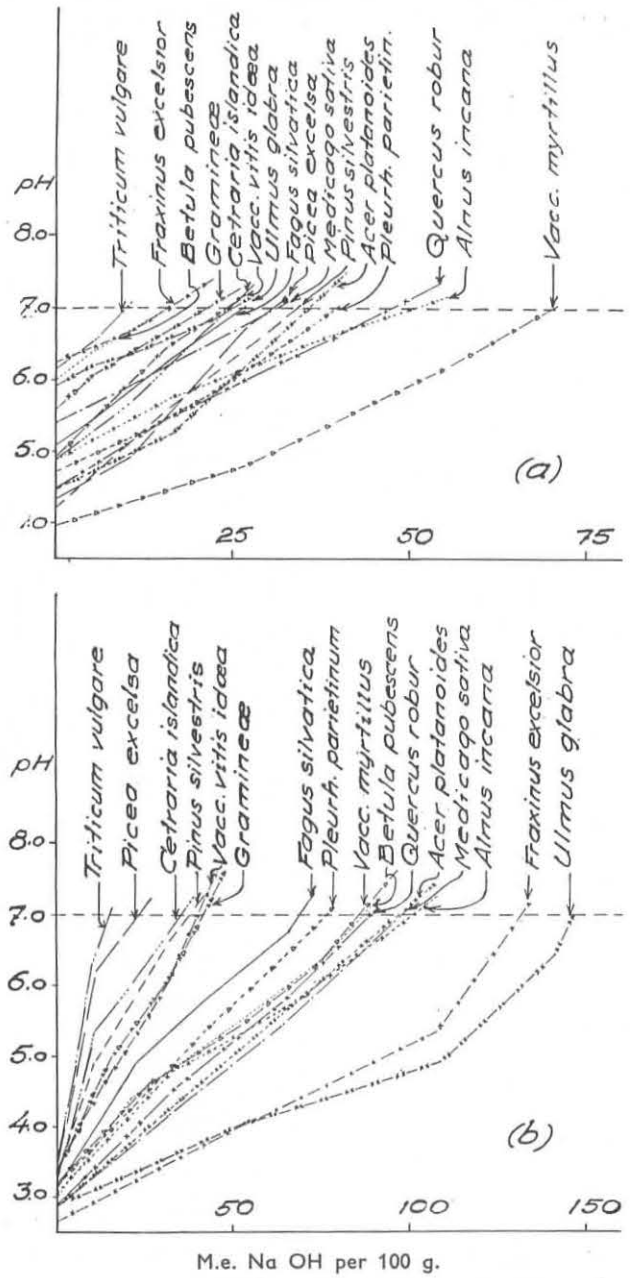

Fig. 5. Titration curves of the original, undecomposed samples; (a) untreated (b) electrodialysed.

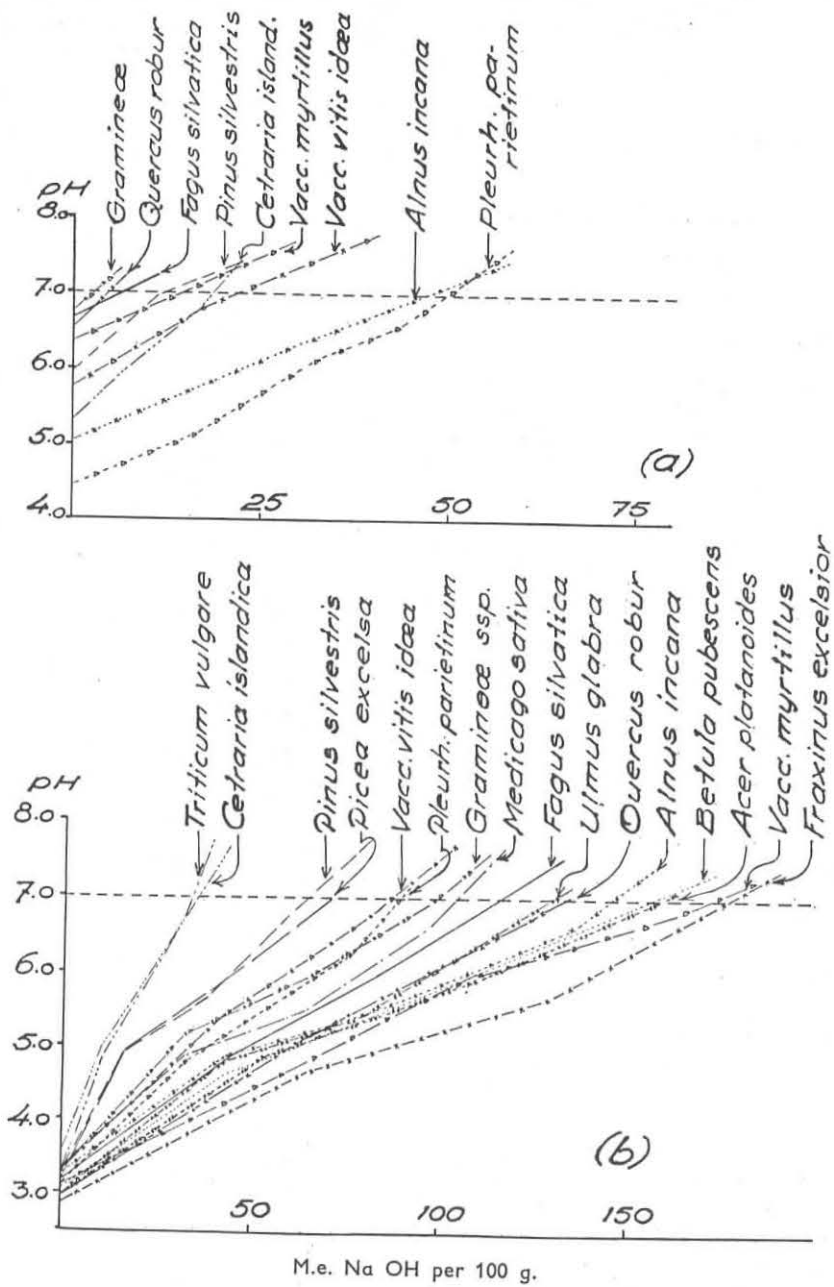

Fig. 6. Titration curves of the transformed (unleached aerobic series) samples; (a) untreated, (b) electrodialysed.

Table 10 a. *The acidoid content (A) in the original and the transformed materials.*

M.e./100 g. dry matter.

Material:	Original	Transformed:					
		Aerobic:			Anaerobic:		
		Leachings cc:					
		None	2400	9600	None	2400	9600
Picea excelsa	26.0	71.0	56.7	60.0	35.2	28.7	25.5
Pinus silvestris	37.7	65.2	64.2	70.0	40.2	37.0	36.2
Fagus silvatica	68.5	116.0	115.8	115.6	74.6	69.2	66.0
Betula pubescens	87.0	156.6	149.0	135.0	88.7	79.0	66.5
Average 4:	54.8	102.2	96.4	95.2	59.7	53.5	48.6
Fraxinus excelsior	131.5	175.6	161.1	145.2			
Alnus incana	100.0	145.8	126.0	119.7			
Ulmus glabra	147.0	130.0	123.0	121.5			
Quercus robur	89.5	132.6	135.5	134.2			
Acer platanoides	97.0	157.2	167.0	154.0			
Vaccinium myrtillus	86.5	171.0		111.5			
Vaccinium vitis idaea	40.7	87.3		75.8			
Pleurhozium parietinum	76.7	89.1		71.0			
Cetraria islandica	35.2	36.0	28.6	25.6			
Gramineae	41.0	99.0		73.5			
Triticum vulgare	15.0	34.3		21.1	18.0		10.5
Medicago sativa	96.5	104.3	79.0	70.2	36.0		26.2
Average 16:	73.5	110.7		94.0			

tralize the acidoids and acids to pH 7, and the very weak acidoids and acids which only bind base at higher pH than 7 do not concern us here. The absence of figures in the table does not mean that no organic acids were present but that they could not be calculated. As a matter of fact the transformed, alkaline materials contain more acids than the acidic materials just as the original materials possessing a high pH, such as ash and elm, also possess a high content of organic acids. This was very evident from the titration values of the anode solution. (We do not here present the titrations values of the anode nor of the cathode solutions because we consider them less accurate than the values here employed.)

The most significant about the data in table 11 is:

1. that the quantities of organic acids in the original materials show a general relationship to the quantities of bases (cf. fig. 7); and
2. that the acids are greatly reduced in the transformed materials, anaerobic as well as aerobic, unleached as well as leached.

A notable exception to the last rule is found in the case of the

Table 10 b. *The acidoid content in the original and transformed materials.*

M.e./100 g. Loss on ignition.

Material	Original	Transformed:					
		Aerobic:			Anaerobic:		
		Leachings cc:					
		None	2400	9600	None	2400	9600
Picea excelsa	26.3	72.3	57.5	60.8	35.5	28.9	25.6
Pinus silvestris	38.0	66.1	65.1	71.1	40.6	37.2	36.5
Fagus silvatica	70.5	122.2	120.9	122.2	76.9	71.0	67.0
Betula pubescens	87.6	158.2	150.8	137.2	89.4	79.4	66.8
Average 4:	55.6	104.7	98.6	97.8	60.6	54.1	49.0
Fraxinus excelsior	134.1	185.0	171.1	152.5			
Alnus incana	101.9	149.2	129.8	124.8			
Ulmus glabra	181.5	202.1	189.3	190.0			
Quercus robur	91.7	137.5	140.8	138.4			
Acer platanoides	101.9	171.8	182.5	167.2			
Vaccinium myrtillus	87.5	173.9		114.8			
Vaccinium vitis idaea	40.9	87.9		76.4			
Pleurhozium parietinum	79.3	93.7		77.4			
Cetraria islandica	35.4	36.6	28.9	25.9			
Gramineae	43.3	119.1		90.8			
Triticum vulgare	16.1	37.9		23.1	19.5		11.2
Medicago sativa	105.2	107.7	82.1	72.3	36.5		26.4
Average 16:	77.6	120.1		102.8			

unleached alder with its 58.7 m.e. acids. This can be ascribed to the accumulation of nitric acid.

The three negative values in the table might be accounted for by acidoids included in the A values but originally in combination with Fe or Al, not all of which are included in the B values.

Acidoid + acid/base: In the original material this ratio (cf. table 12) is lowest in the ash (1.06) and is < 1.60 in every leave-litter, in wheat straw, in grass and in lucern hay. The lichens show by far the highest ratio (3.88). The ratios are much lower in the transformed materials (leached, anaerobic wheat straw excepted). Where the ratio is < 1.0 the pH is > 7.0 (cf. table 7). The ratio is therefore lowest in birch, ash, elm, maple and lucern hay in all of the aerobic series and in birch, wheat straw and lucern hay in the unleached anaerobic series.

The correlation between acidoids, acids and bases in the original material is shown in fig. 7.

In view of the relatively narrow range of pH this correlation

Table 11. *Organic acids (a) in the original and the transformed material.* $a = H + B - A$.

M.e./100 g. dry matter.

Material	Original	Transformed: Aerobic: Leachings cc: None	2400	9600	Anaerobic: Leachings cc: None	2400	9600
Picea excelsa	49.7	—3.2	30.5	14.7	14.0	6.4	4.0
Pinus silvestris	39.4	18.3	17.2	29.3	15.4	9.4	7.8
Fagus silvatica	34.0	2.7	—7.9	4.0	15.0	7.0	2.7
Betula pubescens	69.4						
Average 3:	41.0	5.9	13.3	16.0	14.8	7.6	4.8
Fraxinus excelsior	148.9						
Alnus incana	39.3	58.7	16.3	30.4			
Ulmus glabra	139.0						
Quercus robur	57.8	52.8	39.2	31.3			
Acer platanoides	74.8						
Vaccinium myrtillus	45.6	2.6		14.1			
Vaccinium vitis idaea	19.3	4.7		3.0			
Pleurhozium parietinum	4.3	27.8		20.6			
Cetraria islandica	—1.8	2.3	0.0	5.1			
Gramineae	21.2	4.4		7.4			
Triticum vulgare	34.3			11.2			1.8
Medicago sativa	97.8						7.7
Average 7:	26.5	21.9		16.0			

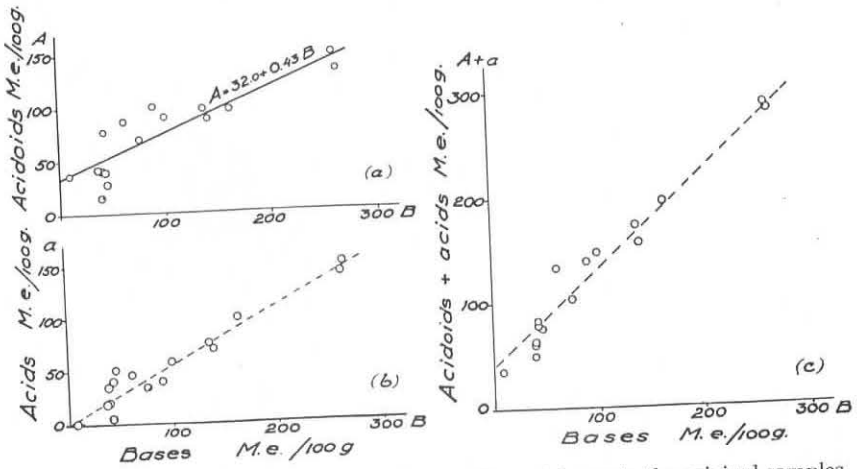

Fig. 7. The relationship between acidoids, acids and bases in the original samples.

Table 12. *The acid/base ratio* $[A + a/B\ (= H + B/B)]$ *in the original and transformed material.*

Material	Original	Transformed: Aerobic: Leachings cc: None	2400	9600	Anaerobic: Leachings cc: None	2400	9600
Picea excelsa	1.68	1.00	1.03	1.04	1.08	1.25	1.38
Pinus silvestris	1.78	1.20	1.16	1.51	1.17	1.28	1.40
Fagus silvatica	1.35	1.06	1.11	1.12	1.08	1.14	1.17
Betula pubescens	1.11	<1.0	<1.0	<1.0	<1.0	1.06	1.23
Average 3:	1.60	1.09	1.10	1.22	1.11	1.22	1.32
Fraxinus excelsior	1.06	<1.0	<1.0	<1.0			
Alnus incana	1.55	1.30	1.15	1.05			
Ulmus glabra	1.10	<1.0	<1.0	<1.0			
Quercus robur	1.47	1.05	1.04	1.04			
Acer platanoides	1.26	<1.0	<1.0	<1.0			
Vaccinium myrtillus	2.13	1.09		1.12			
Vaccinium vitis idaea	1.67	1.31		1.34			
Pleurhozium parietinum	1.95	1.73		1.33			
Cetraria islandica	3.88	1.96	3.01	2.22			
Gramineae	1.54	1.06		1.28			
Triticum vulgare	1.25	<1.0		1.22	<1.0		2.02
Medicago sativa	1.19	<1.0		<1.0	<1.0		1.17
Average 7:	2.03	1.36		1.34			

between the acidic and basic constituents is to be expected. The 39.5 m.e. of base in wheat straw (pH = 6.14) and the 261 m.e. in elm leaves (pH = 5.91) must be compensated by approximately equivalent quantities of acidoids and acids. We are obviously here confronted with one of those compensatory processes in which one form of action calls forth its counter-action according to the principle of Le Chatelier.

But the question arises, which is the horse and which the cart, the acid or the base? Which of the two appears first on the arena? The bases come from the soil whereas the organic acids are formed within the plants. On might therefore ask: does the elm take up a large amount of bases because it synthesizes a large amount of acids and acidoids or does it synthesize the acids and acidoids because it takes up the bases? We shall attempt to give an answer to this question in later papers of this series dealing with the formation and functions of the plant acidoids.

The ultimate pH (= pH_u).

The pH_u of the completely electrodialysed materials in water and in N KCl solution (1 : 10) are shown in tables 13 and 14.

The $pH_{u(H_2O)}$ values are somewhat higher in the V than in the F_0 materials due, perhaps, to the presence of more active basic nitrogen in the former. There is a small increase in pH_u in the anaerobic series and in some of the leached aerobic series. Otherwise there is no definite tendency discernible in these values.

The $pH_{u(KCl)}$ values show an appreciable, general decrease in the aerobic series whereas in the anaerobic series there is little or no change as compared to the original material.

Fig. 8 shows the relationship between the $pH_{u(KCl)}$ values and the acidoid content. Most of the points lie on a curve which expresses a linear relationship according to the equation:

$$(H^+) = kA$$

where k is a constant, A the acidoid content in terms of equivalents per liter and (H^+) the hydrogen ion activity. The scattered points high above the curve represent the V-materials and materials with a high total nitrogen content such as alder and ash leaves and grass.

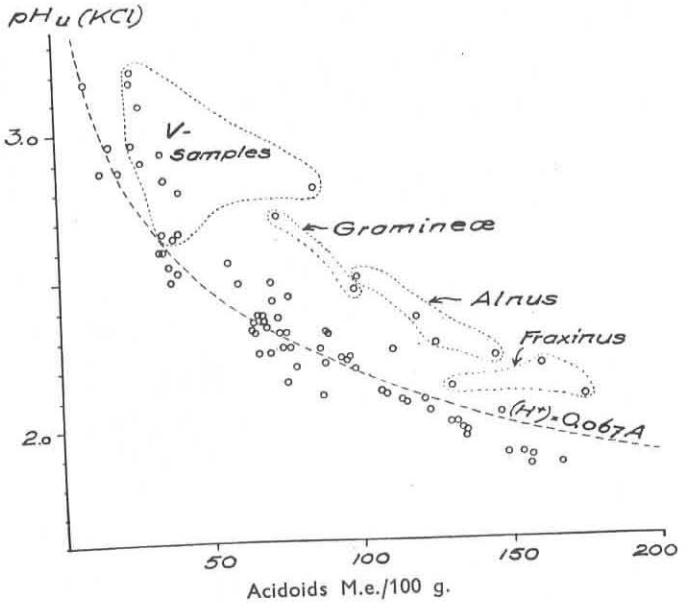

Fig. 8. The relationship between the $pH_{u(KCl)}$ values and the acidoid content of original and transformed samples.

Table 13. *The pH of the electrodialysed material* (pH_u) *in water.*

Material:	Original	Transformed:					
		Aerobic:			Anaerobic:		
		Leachings cc:					
		None	2400	9600	None	2400	9600
Picea excelsa	3.45	3.17	3.24	3.29	3.47	3.51	3.57
Pinus silvestris	3.22	3.27	3.28	3.09	3.28	3.34	3.39
Fagus silvatica	3.11	3.17	3.18	3.15	3.17	3.26	3.29
Betula pubescens	2.99	3.05	3.05	3.05	3.18	3.14	3.23
Average 4:	3.19	3.17	3.19	3.15	3.28	3.31	3.37
Fraxinus excelsior	2.66	2.87	3.12	3.08			
Alnus incana	3.04	3.24	3.24	3.37			
Ulmus glabra	2.90	2.98	3.11	3.08			
Quercus robur	2.90	2.98	2.97	3.01			
Acer platanoides	2.87	2.97	3.11	3.07			
Vaccinium myrtillus	3.18	3.09		3.35			
Vaccinium vitis idaea	3.37	3.28		3.47			
Pleurhozium parietinum	3.14	3.14		3.47			
Cetraria islandica	3.18	3.54	3.79	3.75			
Gramineae	3.33	3.29		3.51			
Triticum vulgare	3.50	3.28		3.84	3.64		3.95
Medicago sativa	2.87	3.31	3.47	3.42	3.91		3.84
Average 16:	3.11	3.16		3.31			

This relationship will be discussed later in connection with a special investigation on the strength of humus acidoids.

The exchange acidity or the difference between the $pH_{u(H_2O)}$ and $pH_{u(KCl)}$ is shown in table 15. This difference is lowest in the original materials, is highest in the aerobic series and intermediate in the anaerobic series. A low exchange acidity means a relatively strong basoid group (basic nitrogen), i. e., a relatively high isoelectric point. This problem will also be reserved for discussion in a later paper.

Decomposition in relation to the acid-base conditions.

Table 16 shows the percentage decomposition of organic matter in the unleached aerobic series and the pH and composition of the original materials.

Broadfoot and Pierre (1939) who studied the decomposition of 31 different kinds of tree litter found a high degree of correlation between percentage decomposition and water soluble organic matter during the first two months and between percentage decomposition and excess base during the following four months. As far as the mature litter (cf. table 1) in our experiment is concerned an examina-

Table 14. *The pH of the electrodialysed materials in N KCl solution.*

Material	Original	Transformed:					
		Aerobic:			Anaerobic:		
		Leachings cc:					
		None	2400	9600	None	2400	9600
Picea excelsa	3.21	2.43	2.56	2.49	2.93	3.09	3.17
Pinus silvestris	2.50	2.32	2.33	2.25	2.53	2.55	2.55
Fagus silvatica	2.36	—	—	2.07	2.27	2.34	2.38
Betula pubescens	2.26	1.85	1.89	1.95	2.21	2.20	2.25
Average 3:	2.66	2.20	2.26	2.23	2.56	2.61	2.66
Fraxinus excelsior	2.12	2.08	2.19	—			
Alnus incana	2.50	2.22	2.27	2.36			
Ulmus glabra	2.03	2.00	2.04	2.08			
Quercus robur	2.31	2.00	1.97	1.98			
Acer platanoides	2.23	1.88	1.85	1.89			
Vaccinium myrtillus	2.80	—		2.25			
Vaccinium vitis idaea	2.66	2.10		2.15			
Pleurhozium parietinum	2.44	2.32		2.49			
Cetraria islandica	2.66	2.84	2.90	2.96			
Gramineae	2.80	2.46		2.71			
Triticum vulgare	2.87	2.60		2.87	2.96		3.17
Medicago sativa	—	—	—	—	3.32		3.03
Average 8:	2.46	2.19	2.23	2.25			

tion of table 16 will at once reveal that a certain degree of correlation exists between the percentage decomposition and the content of bases, acidoids and acids.

Fig. 9 brings out the relationship between percentage decomposition and the content of bases, acids and acidoids in the case of nine F_0 materials (cf. table 16, pine to maple and wheat straw).

Now since there is a correlation between acids and bases, and acidoids and bases it is obvious that where one shows a correlation the other must do the same whether there is a direct relationship or not. It is under such conditions difficult to decide where the correlation is direct and where it is indirect.

We believe, however, that the correlations shown in fig. 9 are direct in both cases and for the following reasons:

1. A high base content means a high content of mineral nutrients and must therefore favor the activity of the microorganisms.

2. A high acidoid content means a high oxygen content and the higher the latter the greater the decomposability of the organic matter. Besides, there seems to be a definite relationship between the acidoid and nitrogen content but this will be reserved for discussion later.

Table 15. *The difference between $pH_{u(H_2O)}$ and $pH_{u(KCl)}$.*

Material	Original	Transformed:					
		Aerobic:			Anaerobic:		
		Leachings cc:					
		None	2400	9600	None	2400	9600
Picea excelsa	0.24	0.74	0.68	0.80	0.54	0.42	0.40
Pinus silvestris	0.72	0.95	0.95	0.84	0.75	0.79	0.84
Fagus silvatica	0.75	—	—	1.08	0.90	0.92	0.91
Betula pubescens	0.73	1.20	1.16	1.10	0.97	0.94	0.98
Average 3:	0.56	0.96	0.93	0.91	0.75	0.72	0.74
Fraxinus excelsior	0.54	0.79	0.93	—			
Alnus incana	0.54	1.02	0.97	1.01			
Ulmus glabra	0.87	0.98	1.07	1.00			
Quercus robur	0.59	0.98	1.00	1.03			
Acer platanoides	0.64	1.09	1.26	1.18			
Vaccinium myrtillus	0.38	—		1.10			
Vaccinium vitis idaea	0.71	1.18		1.32			
Pleurhozium parietinum	0.70	0.82		0.98			
Cetraria islandica	0.52	0.70	0.89	0.79			
Gramineae	0.53	0.83		0.80			
Triticum vulgare	0.63	0.68		0.97	0.68		0.78
Medicago sativa	—	—	—	—	0.59		0.81
Average 8:	0.61	0.96	1.00	0.97			

Table 16. *The relationship between decomposition (aerobic without leaching) of organic matter, pH, acidity and composition of the original material.*

Material	Decomposition %	pH	M.e./100 g. dry matter:				$\frac{H+B}{B}$ $\left(=\frac{A+a}{B}\right)$
			Acidity H	Bases B	Acidoids A	Acids: H+B−A= a	
Picea excelsa	46.1	4.32	30.6	45.1	26.0	49.7	1.68
Pinus silvestris	46.1	4.22	33.9	43.2	37.7	39.4	1.78
Fagus silvatica	44.3	5.08	26.3	76.2	68.5	34.0	1.35
Betula pubescens	55.5	5.99	16.0	140.4	87.0	69.4	1.11
Fraxinus excelsior	70.6	6.24	16.2	264.2	131.5	148.9	1.06
Alnus incana	49.1	4.89	49.2	90.1	100.0	39.3	1.55
Ulmus glabra	65.1	5.91	25.0	261.0	147.0	139.0	1.10
Quercus robur	45.6	4.48	47.2	100.1	89.5	57.8	1.47
Acer platanoides	57.1	4.49	35.0	136.8	97.0	74.8	1.26
Vaccinium myrtillus	61.9	3.97	70.0	62.1	86.5	45.6	2.13
Vaccinium vitis idaea	49.5	4.93	24.1	35.9	40.7	19.3	1.67
Pleurhozium parietinum	34.0	4.71	39.4	41.6	76.7	4.3	1.95
Cetraria islandica	57.6	4.89	24.8	8.6	35.2	−1.8	3.88
Gramineae	75.4	5.59	21.7	40.5	41.0	21.2	1.54
Triticum vulgare	46.5	6.14	9.8	39.5	15.0	34.3	1.25
Medicago sativa	78.3	5.40	31.5	162.8	96.5	97.8	1.19

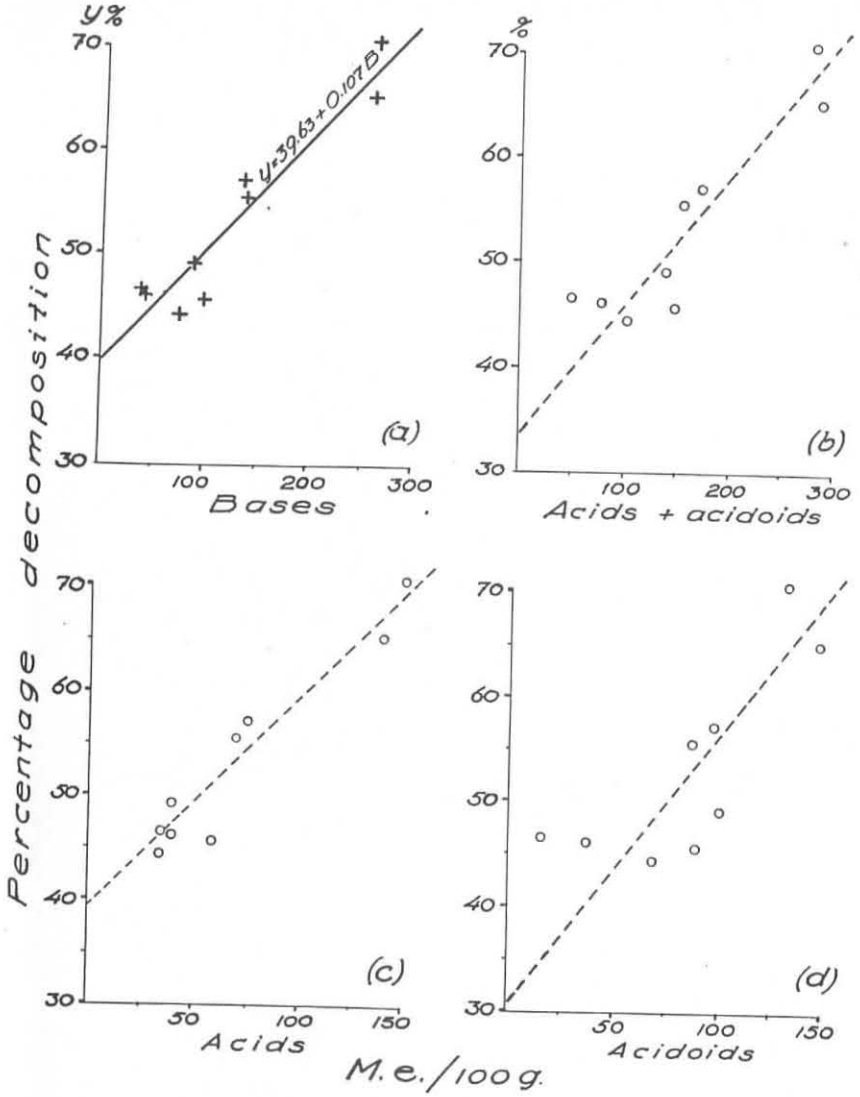

Fig. 9. The relationship between the percentage decomposition and the content of bases, acids and acidoids in nine F_0 samples.

At present it is impossible to decide which of the two factors, base or acidoid content, is the most important for the decomposition. The various kinds of straw (wheat, rye, barley, oath, clover and pea) differ greatly in acidoid and base content and in the rate of decomposition. Will their decomposition be equally rapid at equal base and nutrient salt content? On the basis of still incomplete results the answer is no. It might be added that completely electrodialysed elm leaves containing a mere trace of bases but a very high acidoid content decompose very rapidly in spite of the very low initial pH of 2.90.

We have shown that the diffusible organic acids belong to the most easily decomposed components of the litter (cf. table 11) and that the water soluble organic matter, consisting largely of organic acids, rapidly decreases during the first few months (cf. fig. 1—4). The correlation between water soluble material and decomposition observed by Broadfoot and Pierre during the first two months is thus seen as a correlation between decomposition and the content of easily decomposed substances, largely acidic.

The decomposition of the green V materials such as *Vaccinium myrtillus*, *Cetraria islandica*, *Gramineae* and *Medicago sativa* is evidently dominated by the content of easily decomposed materials and is therefore less influenced by the original percentage of basic and acidic constituents. An easily decomposed material becomes, however, enriched in bases through the »mineralization» provided the latter is not compensated by leaching. A material originally poor in bases may thus become relatively rich (cf. *Vaccinium myrtillus* in table 9). The decomposition will then be a function of a very different base status than that of the original material.

Summary.

Sixteen samples, including mature leaves and needles, straw and green plant materials, have been studied before and after decomposition for one year under aerobic and anaerobic conditions with and without leaching. The materials were examined with respect to changes in their reaction, acidity and content of »excess base», organic acids and acidoids.

The pH increases rapidly in the aerobic series as a result of a decomposition of the organic acids. The higher the excess base (and organic acids) the greater the rise.

Where the bases are low and the leaching intense there is later a decrease in pH due to the formation of acidoids.

In the original material there is a correlation between the excess base and the acids and acidoids, and, in the mature litter, between each of these and the rate of decomposition.

There is a linear relationship between the hydrogen ion activity and the acidoid content of the electrodialysed mature litter or its decomposed residue.

References.

Broadfoot, W. M. & Pierre, W. H., 1929. Forest soil studies: I. Relation of rate of decomposition of tree leaves to their acid-base balance and other chemical properties. — Soil Sci. 48, p. 329—348.

Hesselman, H., 1926. Studien über die Humusdecke des Nadelwaldes, ihre Eigenschaften und deren Abhängigkeit vom Waldbau. — Meddel. Statens Skogsförsöksanst. 22, p. 169—552.

Lunt, H. A., 1935. Effect of weathering on dry matter and composition of hardwood leaves. — Jour. Forestry 33, p. 607—609.

Mattson, S. & Wiklander, L., 1940. The laws of soil colloidal behavior: XXI. The amphoteric points, the pH, and the Donnan equilibrium. — Soil Sci. 49, p. 109—153.

Melin, E., 1930. Biological decomposition of some types of litter from N. American forests. — Ecology 11, p. 72—101.

Plice, M. J., 1934. Acidity, antacid buffering, and nutrient content of forest litter in relation to humus and soil. — Cornell Agr. Exp. Sta., Mem. 166.

(MS. received June 10th 1940.)